Simulations of kinetic events at the atomic scale

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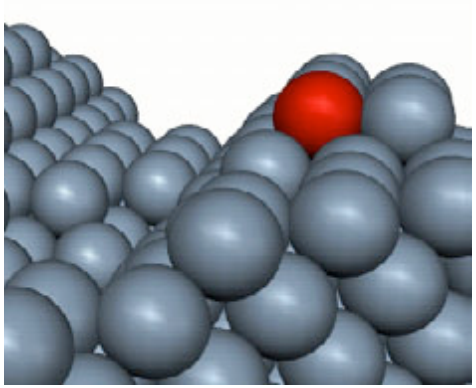
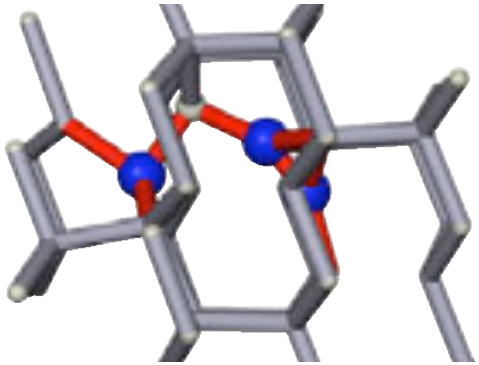
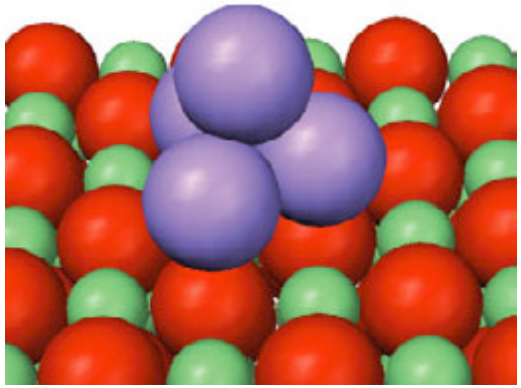
Al / Al(100)



B_3I / Si



Pd / MgO

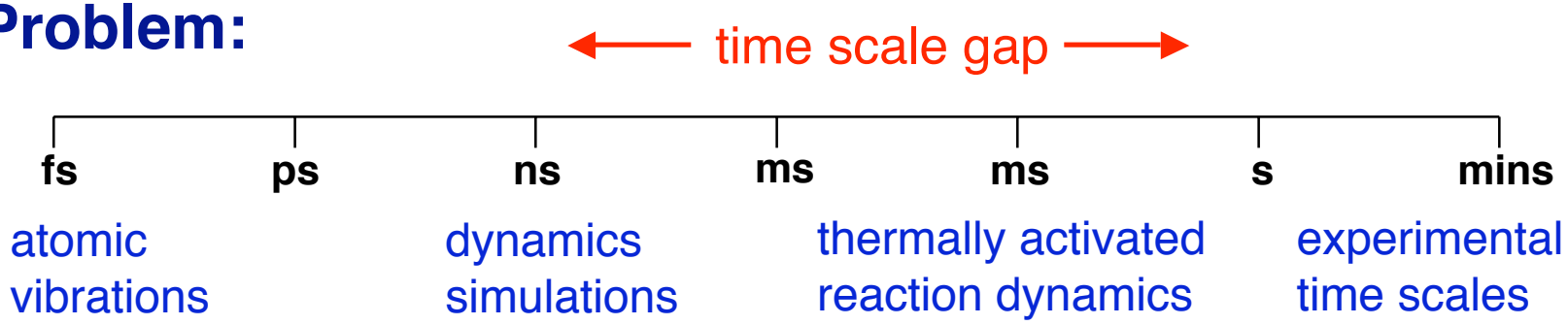


How can we simulate the dynamics of molecular systems over experimental time scales?

Objective:

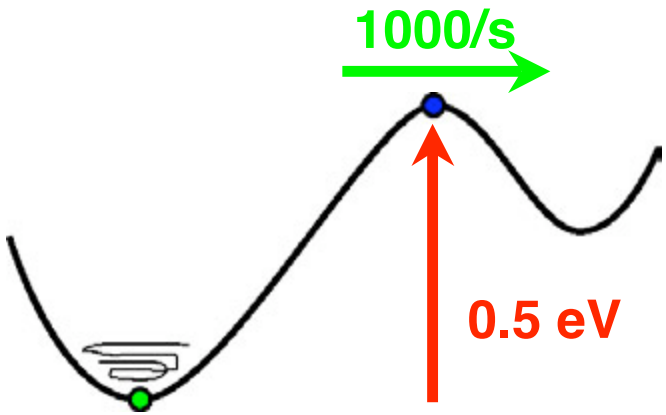
To calculate dynamics of a surface over time scales which are much longer than can be calculated with direct classical dynamics.

Problem:



Most interesting transitions are rare events (much slower than vibrations)

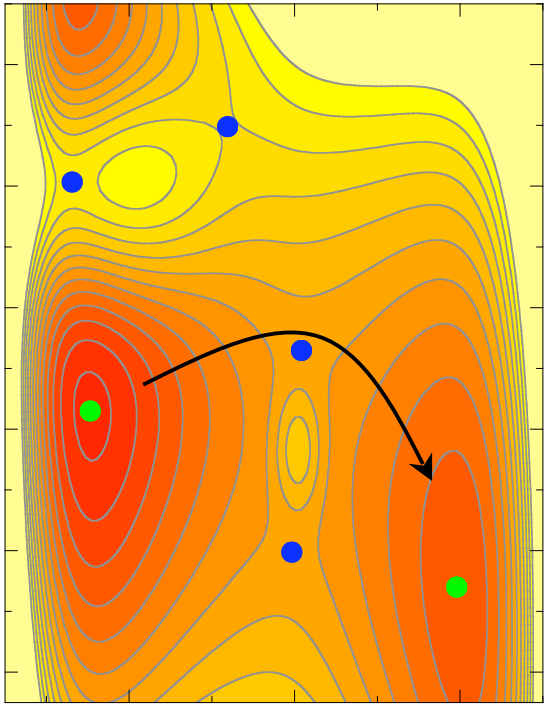
Simulating a transition for a typical rare event with classical dynamics can require ~10^{12} force evaluations



Transition state theory

A statistical theory for calculating the rate of slow thermal processes

The primary task is to find an N-1 dimensional dividing surface that represents a bottle neck for the transition



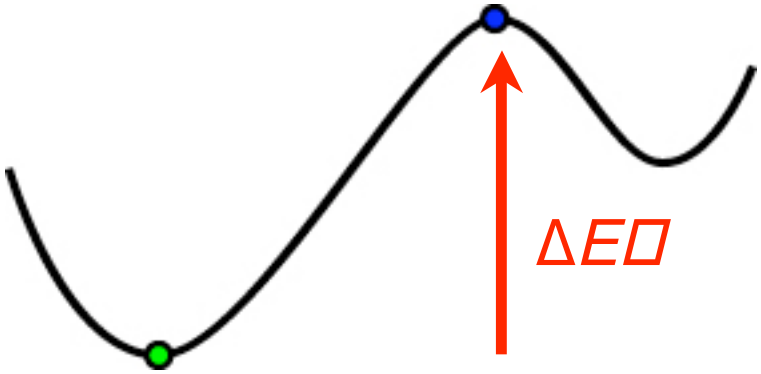
Minima
Saddle Point

Harmonic transition state theory

Need to find saddle points on the energy surface

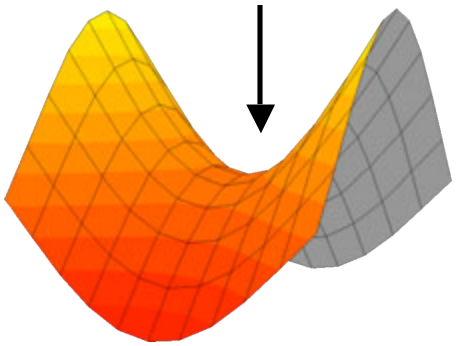
Rate of escape through each saddle point region:

$$Rate = \frac{\prod_{i=1..N} \nu_i}{\prod_{j=1..N-1} \nu^{\ddagger}_j} \cdot e^{-\frac{\Delta E}{k_B T}}$$

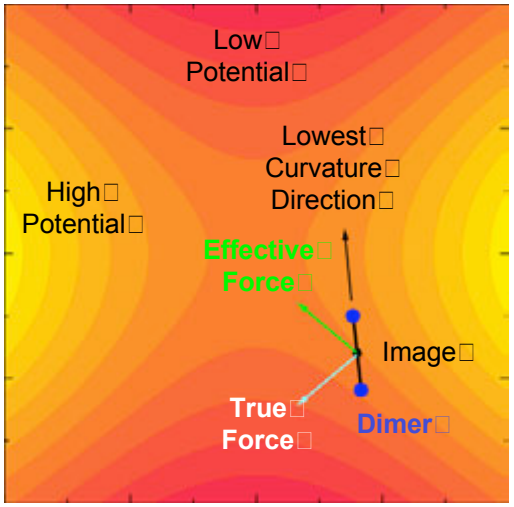


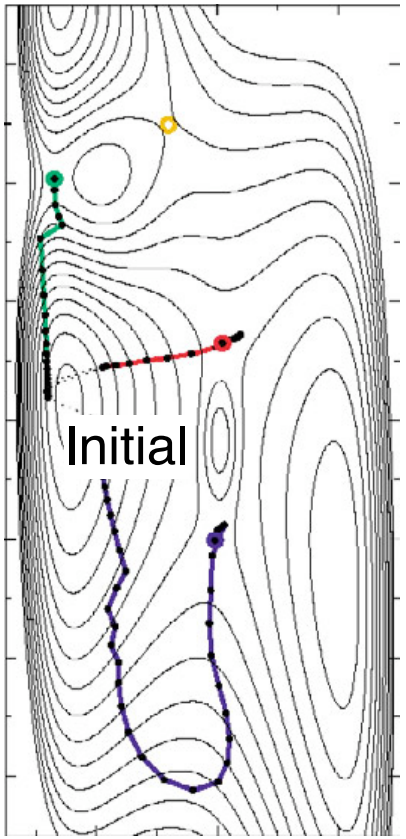
Methods for determining reaction rates

Finding Saddle points

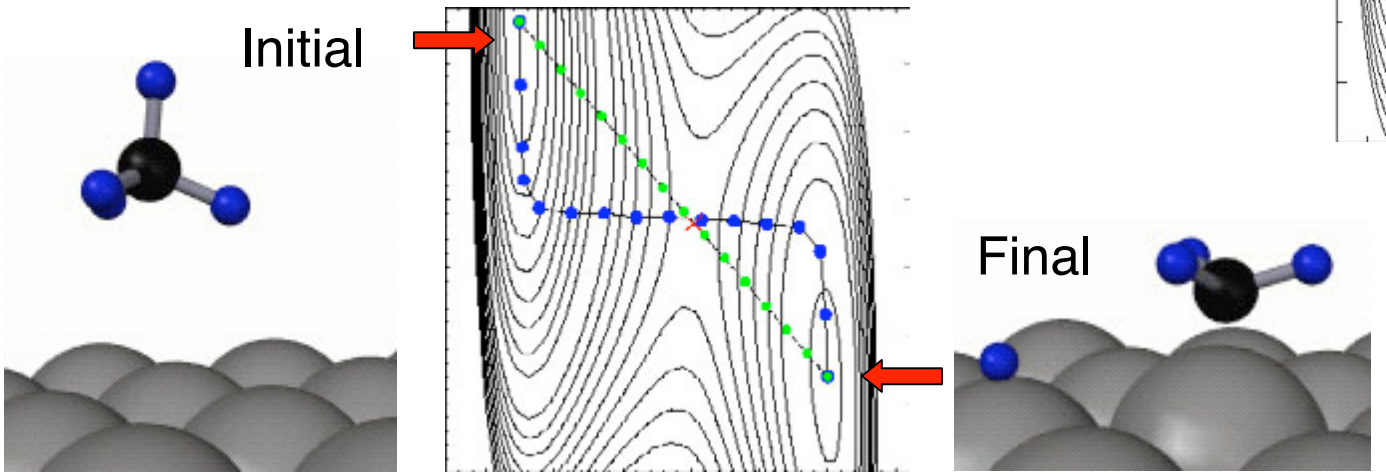


Single Ended:





Double Ended:



The Nudged Elastic Band Method

Recent developments:

- Improved tangent
- Climbing image
- Double nudging (Wales)

- Second order optimizers
  - conjugate gradients
  - quasi-newton (bfgs)
- Internal coordinates
- Rigid constraints (string method)

Force on each image:

$$\vec{F}_i^{nudged} = -\vec{\nabla}V(\vec{R}_i)|_\perp + \vec{F}_i^s \cdot \hat{\tau}_\parallel \, \hat{\tau}_\parallel$$

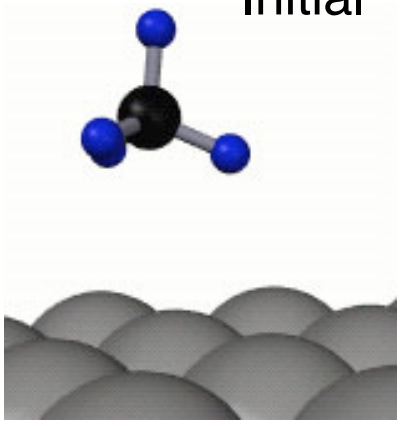
potential

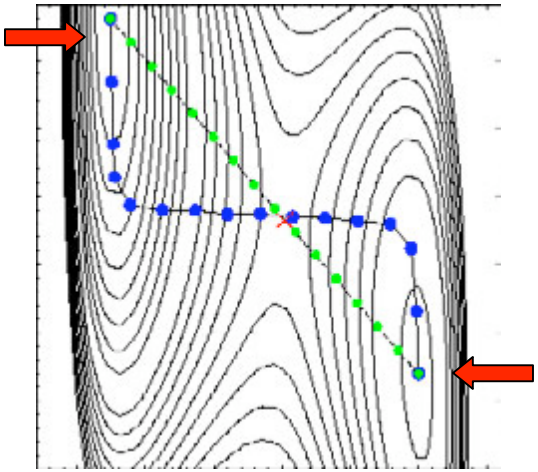
$$\vec{\nabla}V(\vec{R}_i)|_\perp = \vec{\nabla}V(\vec{R}_i) - \vec{\nabla}V(\vec{R}_i) \cdot \hat{\tau}_\parallel \, \hat{\tau}_\parallel$$

$$\vec{F}_i^s \equiv k_{i+1}\left(\vec{R}_{i+1} - \vec{R}_i\right) - k_i\left(\vec{R}_i - \vec{R}_{i-1}\right)$$

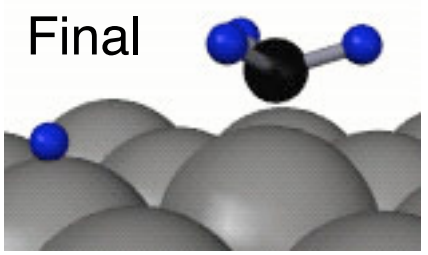
springs

Initial





Final



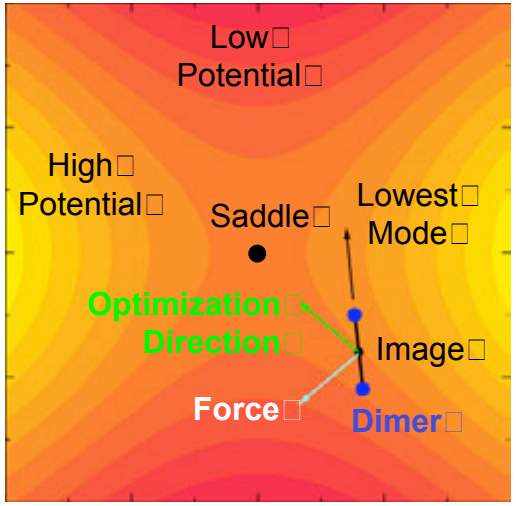
Minimum mode following methods

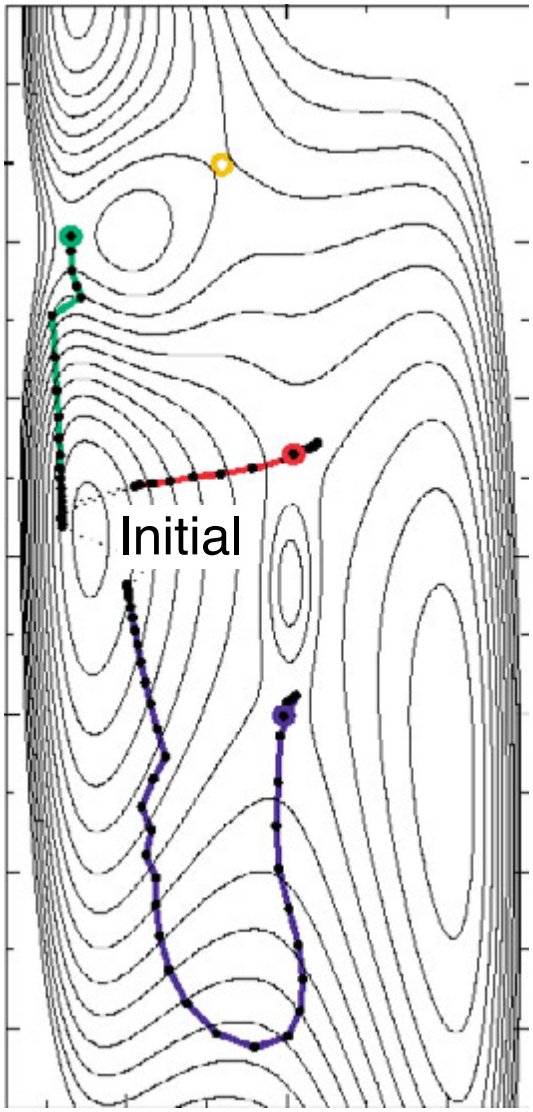
Dynamics: know the initial state, but don't know the final state!

- Find the lowest curvature mode
  - Dimer method (Voter, Henkelman, Jónsson)
  - Lanczos (Barkema, Mousseau)
  - Langrange multipliers (Wales)

- Follow the minimum mode up the potential, minimize in all other modes

- Many independent searches can be used to find unknown reaction mechanisms



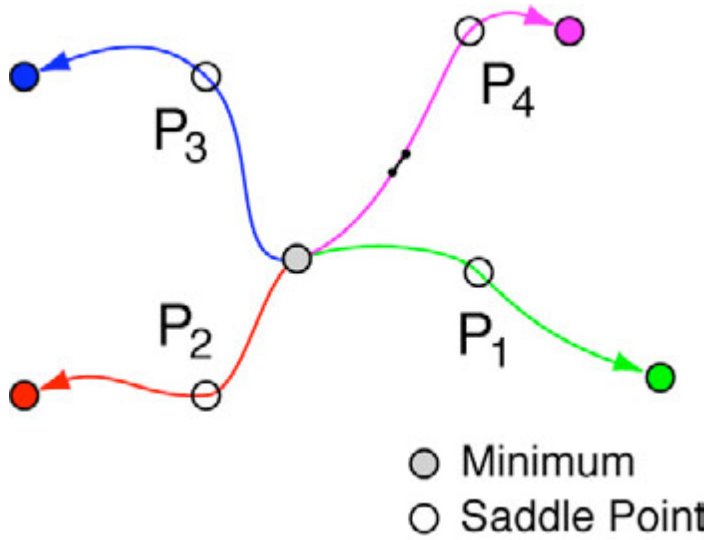


Adaptive kinetic Monte Carlo

Combine saddle point searches with kinetic Monte Carlo (KMC):

Standard KMC

1. Find low energy saddle points using a min-mode method.
2. Choose one processes from a Boltzman distribution.
3. Hop to the final state of the chosen process.
4. Increment time by an average amount Δt.
5. Repeat.



Probability: $p_i \propto r_i$

Rate: $r_i = \nu\, e^{-\Delta E_i / k_B T}$

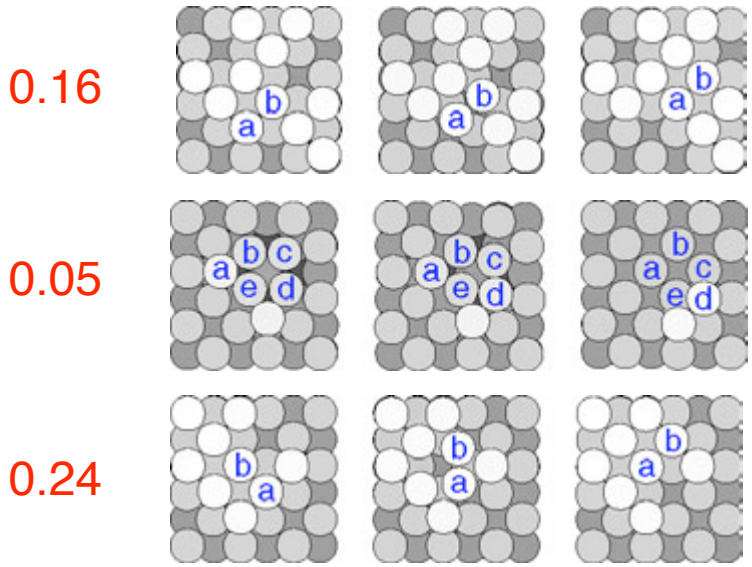
Time: $\overline{\Delta t} = \dfrac{1}{\sum r_i}$

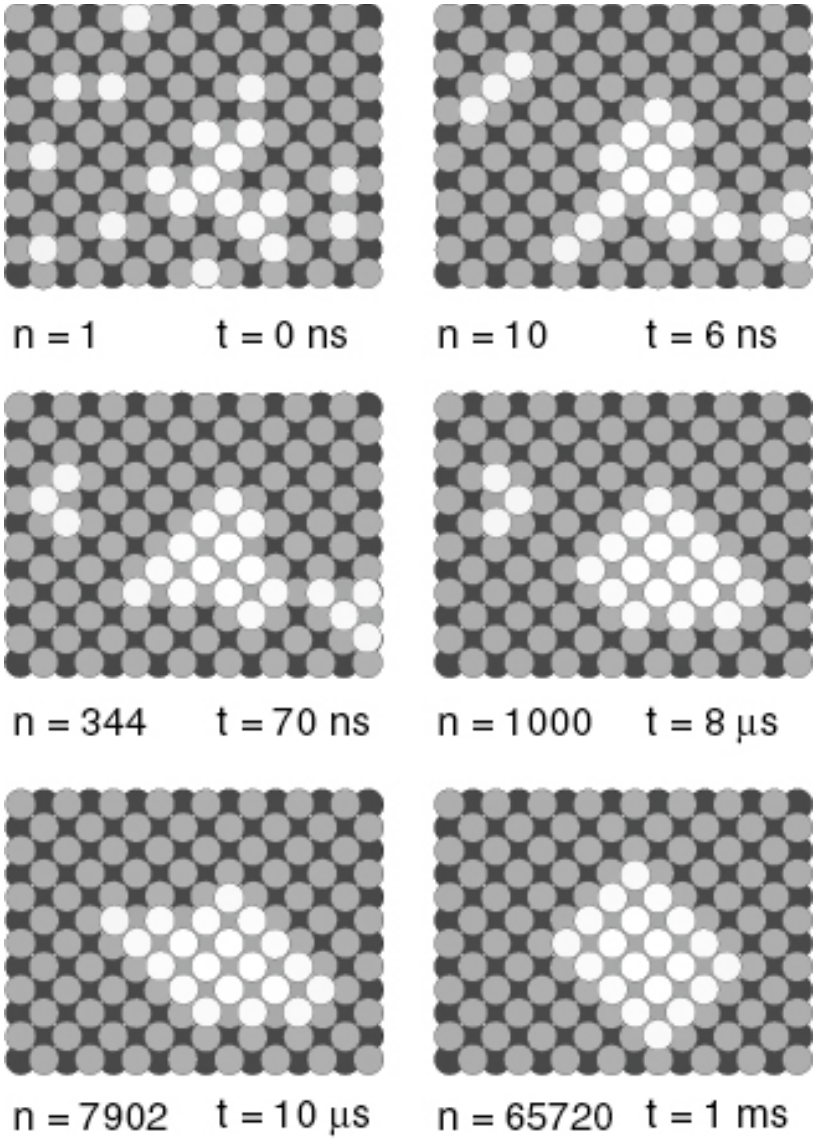
Al / Al(100) ripening

Complex events do happen

- A compact island forms in 1 ms at 300K
- Find many events which are not included in standard KMC event tables

ΔE (eV) **Events**

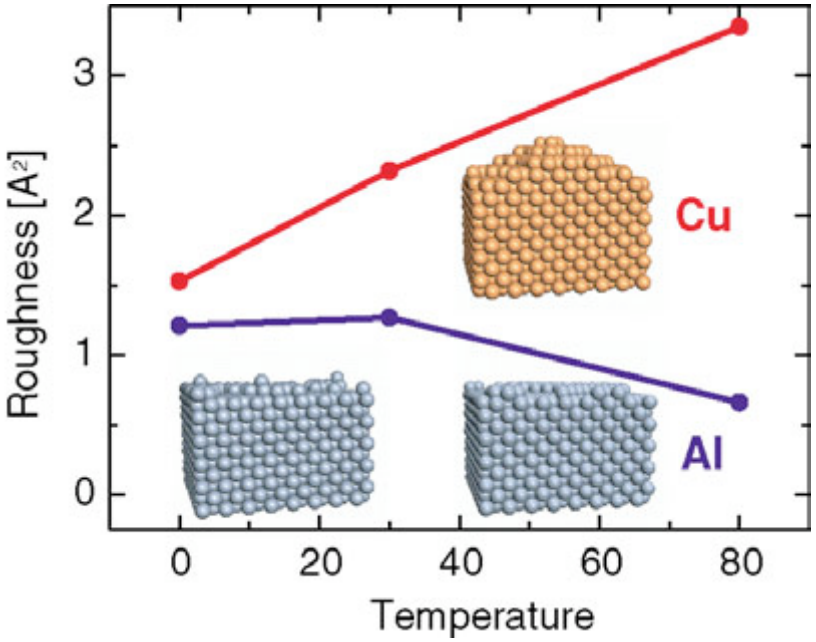


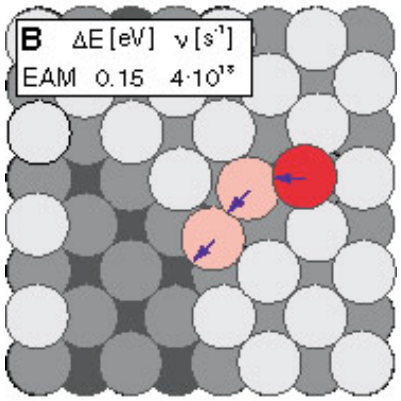


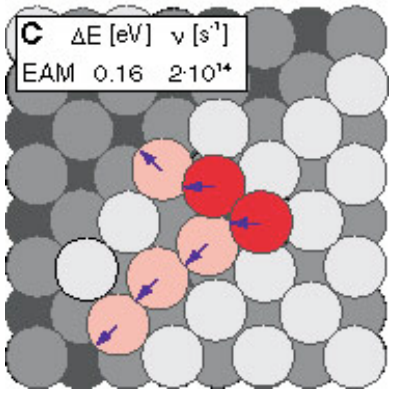
Al / Al(100) growth

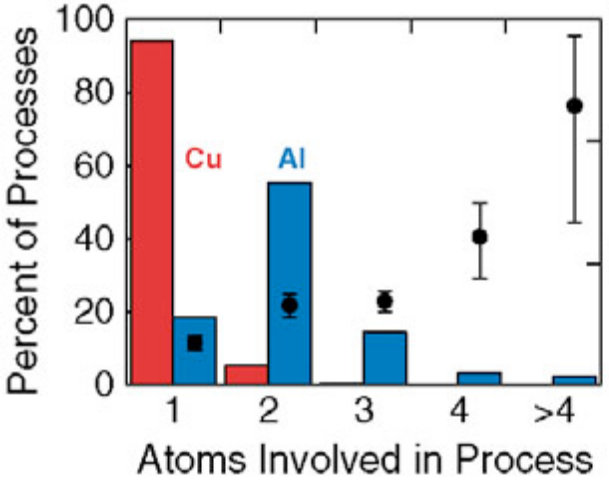
Multi-atom events can be important for dynamics

- Exchange events involving more than one atom lead to smooth growth on Al at 77K
- Single atom ripening events contribute to rough growth on Cu





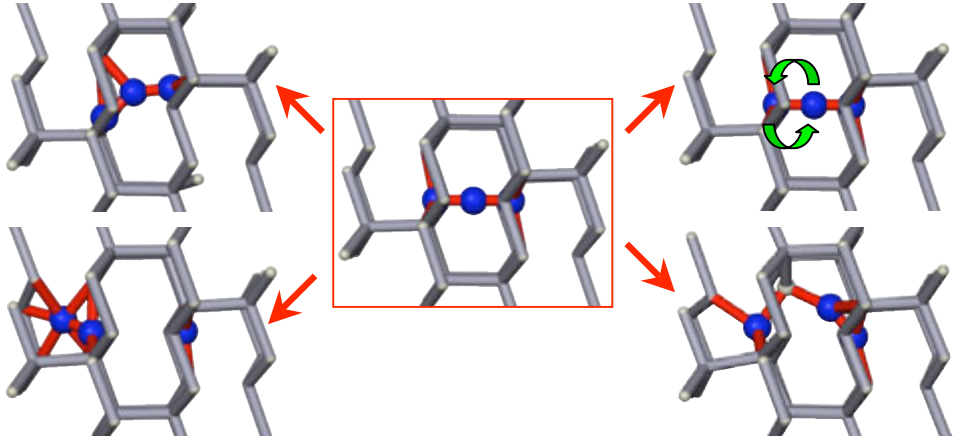


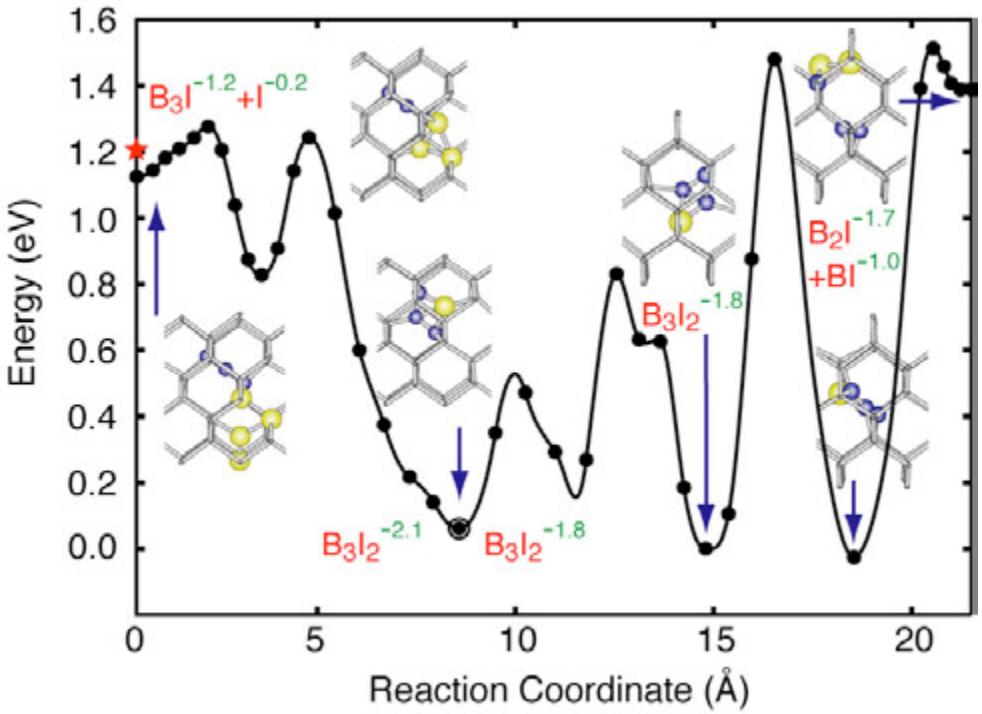


Dynamics from Density Functional Theory

When there is no accurate empirical potential …

- Saddle points can be found directly with DFT.
- Min-mode following methods are in VASP, SIESTA, SOCORRO, and CASTEP
- Only a few tens of saddle point searches are possible in each new state
- Can be used to find unexpected reaction pathways and dynamics

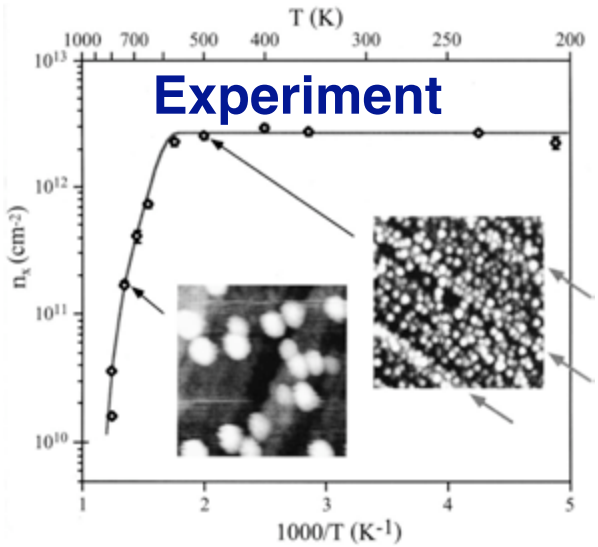


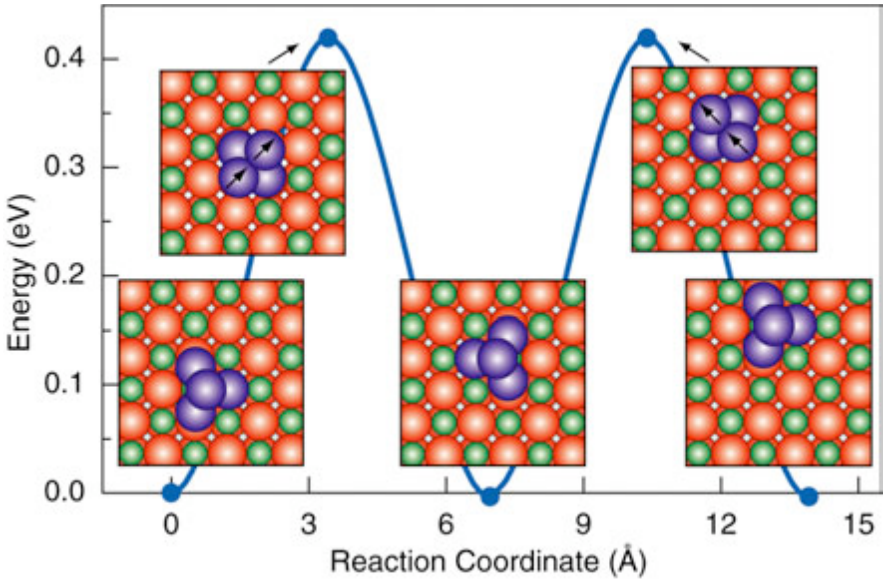


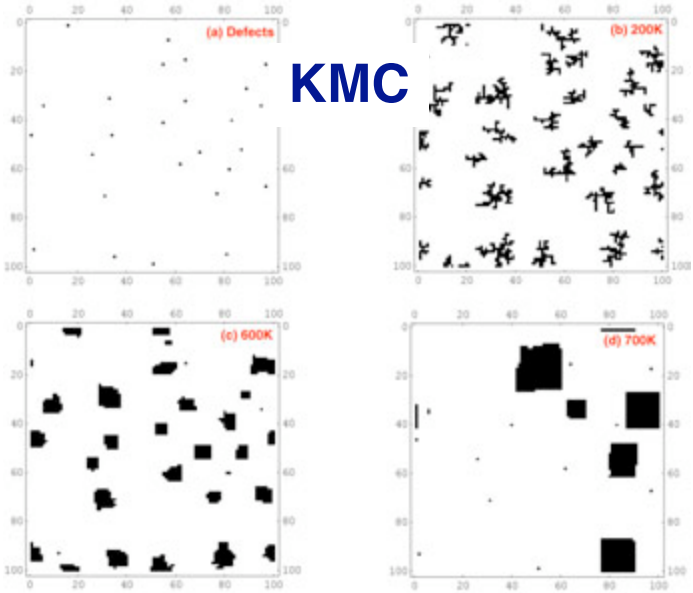
From DFT to kinetic Monte Carlo: Pd / MgO

If all important mechanisms are found, KMC can reach longer time scales

- DFT calculations of Pd diffusion on MgO show that small clusters are more mobile than the Pd monomer
- DFT diffusion rates are used in a KMC simulation to compare with experiment







Application to Hydrogen Storage Materials

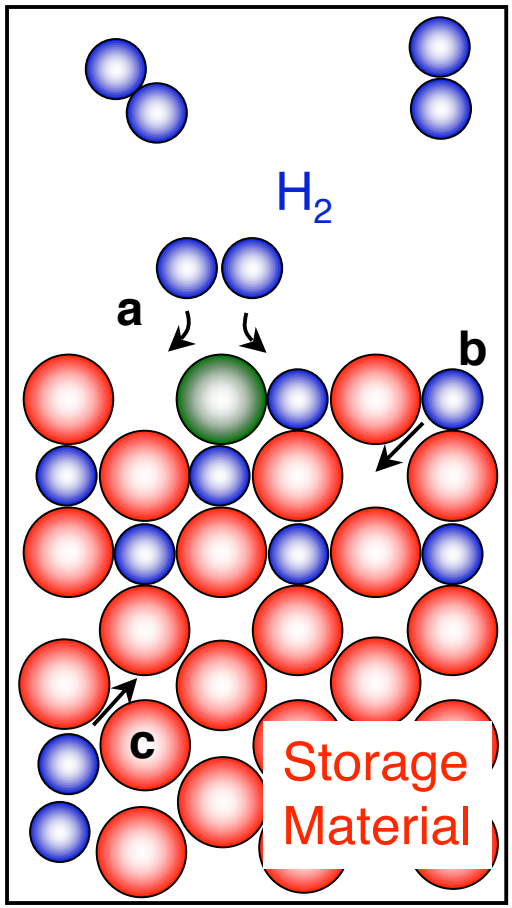
Challenges for simulating the kinetics of hydrogen storage materials

a. Need to develop potentials for modeling H_2 dissociative adsorption at catalysts, or use DFT

b. Since H diffusion barriers will change with environment, it is unlikely that any few reaction mechanisms can be used with standard KMC to model the storage kinetics of a material

c. A phase change in a material will limit the use of traditional kinetic Monte Carlo

Provides an exciting opportunity for new methods!



Quantum effects for hydrogen kinetics

Zero point and tunneling corrections

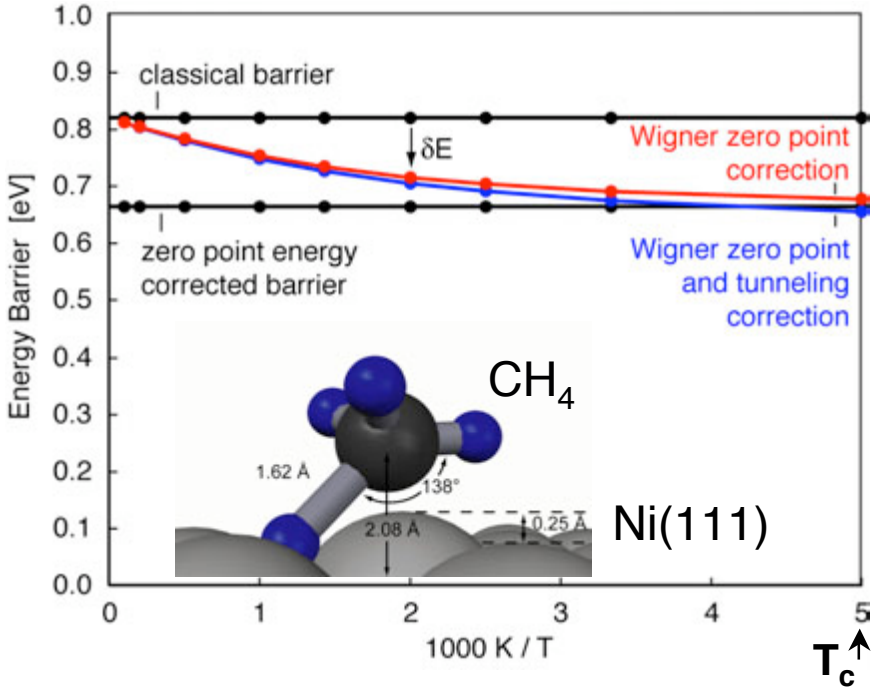
- Estimate using classical normal modes above T_c

$$T_c = \frac{\hbar\,|\nu^*|}{k_B}$$

Wigner correction:

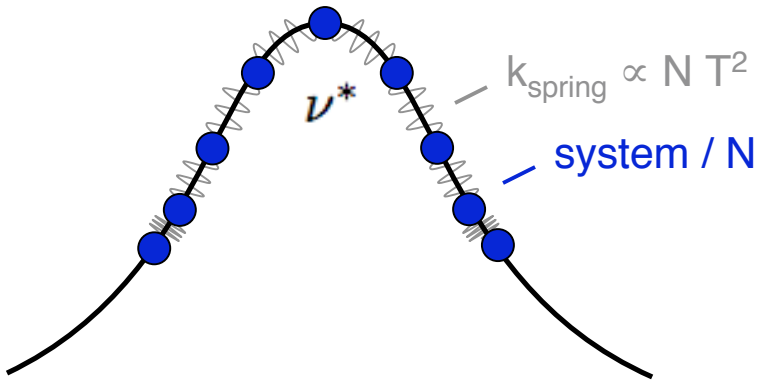
$$\delta E_{\text{wig}} = -k_B T \ln\left[\frac{\Pi_i \sinh(x_i^{\text{init}})/x_i^{\text{init}}}{\Pi_i \sinh(x_i^{\ddagger})/x_i^{\ddagger}}\right]$$

where $x_i = h\nu_i/2k_BT$



- Below T_c, find instanton using Min-mode following methods (Jónsson)

Instanton: Saddle point for Feynman chain to cross the barrier



Adaptive kinetic Monte Carlo

Strengths and weaknesses

- Saddle point searches are independent, and can be computed in a parallel (distributed) environment
- Need to find all important (low energy) reaction mechanisms

  - contrast with accelerated dynamics methods (Voter)
- Accuracy determined by sampling:

  - Fewer searches for expensive (DFT) calculations
  - Extensive sampling when using empirical potentials
- No simple relation between sampling and accuracy
- If the important processes are known, they can be used in a KMC simulation to reach longer time and length scales
- Can include quantum effects as necessary

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-

Collaborators

UT: Lijun Xu, Nathan Froemming, Wenjie Tang, Dan Sheppard

Other groups: Hannes Jónsson (Iceland), Arthur Voter (LANL), Blas Uberuaga (LANL), Charles Campbell (UW)

Freely available software tools

• http://eon.cm.utexas.edu/	The EON distributed computing project
• http://theory.cm.utexas.edu/fida/	FIDA Distributed computing framework upon which eon is built
• http://theory.cm.utexas.edu/vtsttools/	Dimer, NEB, and dynamical matrix methods implemented in the VASP code
• http://theory.cm.utexas.edu/bader/	Bader charge density analysis